



ORIGINAL ARTICLE



Thermal decomposition kinetics of some transition metal coordination polymers of fumaroyl bis (paramethoxyphenylcarbamide) using DTG/DTA techniques

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Abstract In the present work, thermal degradation behaviors of the Zn (II), Cd(II), and Hg(II) coordination polymers of fumaroyl bis (paramethoxyphenylcarbamide) (*fbpmpc*) have been investigated by using thermogravimetric (TG) analysis, differential thermal analysis (DTA) and derivative thermogravimetry (DTG) analysis under non-isothermal conditions in nitrogen atmosphere at multiple heating rates. TG–DTA study noteworthy inferred the presence of lattice water in outer sphere of all the polymers. The decomposition was carried out in three-four well-separated stages where involved the loss of water molecules in the first step followed by organic ligand. Furthermore, the kinetics and thermodynamic stabilities of multi-steps thermal degradation were evaluated.

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The activation energy (E_a), order of reaction (n), Arrhenius factor (A), enthalpy change (ΔH), entropy change (ΔS) and free energy change (ΔG) of coordination polymers were obtained by using the Coats–Redfern (CR) method. Ultimately, based on initial, half and final decomposition temperature, and kinetics parameters values the orders of thermal stability were estimated.

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1. Introduction

Coordination polymer of divalent transition metal with chelating ligand is an interesting topic in the branch of coordination chemistry due to its specific properties and high thermal stability than ordinary complexes. During the last two decades, researchers showed a lot of interest in the coordination chemistry of d^{10} system divalent metal in coordination polymers and organometallic polymers (Carlucci et al., 2003; Rowsell et al., 2004; Kitagawa et al., 2004; Rao et al., 2004). Indeed, divalent metal ions in coordination polymers play noteworthy roles because they enhance thermal stability properties. Instances, metal ions possessing lower or single oxidation state can form more stable coordinated polymers with chelating ligands (Tomic, 1965; Gawas and Verenka, 2015). Recently, metal coordination polymers, containing heterocyclic ring, act as more thermally stable. Besides, all over the globe it is also the subject of great interest to many researchers. Such heterocyclic ring possessing compounds are commonly called as chelate polymers, organometallic polymers or coordination polymer. One of the most important thermally stable compounds in the branch of coordination chemistry is chelate polymer compounds. The high thermal stability of coordination polymers is due to the presence of chelation and heterocyclic ring formation. In our previous work, we reported the ability of chelation in the coordination polymers (Chaudhary et al., 2013a,b). Nevertheless, over the past few decades throughout the world the solid state chemistry was being given great importance by the researchers to identify the water hydration, stability, thermal decomposition of organic moiety in coordination polymers by using various thermal techniques such as thermogravimetry, derivative thermal analysis, differential thermal gravimetry, and differential scanning calorimetry (Mistretta et al., 2014; Al-Maydama et al., 2009; Que and Qiu, 2015; Madej and Szczera, 2015).

Thermal analysis techniques are extremely useful in various fields of sciences. Indeed, a thermal analysis is a valuable technique because researchers are using it to evaluate the thermal decomposition behaviors, melting, stability, kinetic triplet, and thermodynamic parameters. It is also used to compare their thermal stabilities at each step of degradation of various materials such as coordination polymers, chelate polymers, terpolymers, polymer–metal complexes, inorganic polymers, ferrites, sphalerites, composites, complexes, thermoplastic starch, metal salts, complexing agents, citronellyl diesters, medicinal plant leaves, biological active compounds, and nanocrystalline powder (Chang et al., 2000; Naggar et al., 1997; Lacz and Pasierb, 2013; Giurinca and Zaharescu, 2003; Wang et al., 2004; Bora, 2000; Woznicka et al., 2015; Worzakowska, 2014; Biedunkiewicz et al., 2013; Gingi et al., 2015; Vyas and Iron, 2014; Ando et al., 2015; Wu et al., 2014; Sun et al., 2015).

Our previous works on the synthesis of transition metal coordination polymers with chelating ligand (Chaudhary et al., 2015a,b, 2013) were based on stability. Multi-step thermal decomposition mechanism started with loss of water molecules from the outer sphere of attraction and subsequently from inner sphere coordinated water molecules of coordination polymers that lead to a stable anhydrous intermediate. This process followed by removal of intermediates where it undergoes further degradation involving chelating ligand fragmentation, which occurs through multiple steps. Further, we analyzed kinetic triplet and thermodynamics parameters for each step in detail. Keeping this in mind, we have presented here a complete investigation of thermal decomposition of kinetics study under the title coordination polymers by utilizing CR method.

In this work, we have examined thermal study of three novel coordination polymers of d^{10} divalent transition metals. The objective of present work was to describe the comparative thermal behaviors by using TG–DTG and DTA techniques under multiple heating rates. Further, we have evaluated thermal decomposition kinetics and thermodynamic parameters including activation energy, order of reaction, Arrhenius factor, enthalpy change, entropy change and free energy change by using the Coats–Redfern method for each step of degradation curve with the help of TG–DTG and DTA data. Indeed, above techniques were significantly found helpful to check out the thermal stability and to decide whether water molecules were present at either inner or outer sphere of coordination polymers.

2. Experimental

2.1. Synthesis of ligand and coordination polymers

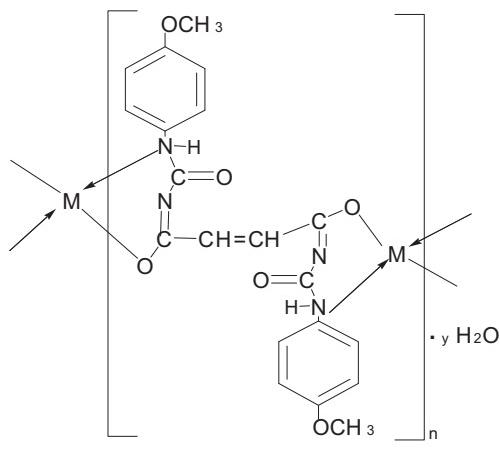
The chelating ligand fumaroyl bis (paramethoxyphenylcarbamide) was first synthesized, spectroscopically characterized and later published (Chaudhary et al., 2012, 2015a,b). The coordination polymers (Fig. 1) of Zn(II), Cd(II), and Hg(II) with fumaroyl bis (paramethoxyphenylcarbamide) were successfully synthesized by using condensation method and characterized by using various standard techniques viz. spectroscopic, microscopic and morphological in order to find out their geometry (Chaudhary et al., 2015a,b).

2.2. Thermal analyses

Thermogravimetric analyses (TG/DTG/DTA) were carried out under nitrogen atmosphere at multiple heating rates of $5\text{ }^{\circ}\text{C}$, $10\text{ }^{\circ}\text{C}$, $15\text{ }^{\circ}\text{C min}^{-1}$ in the range of 28 – $1223\text{ }^{\circ}\text{C}$ at STIC Cochin University Kerala (INDIA). Thermal curves of samples were recorded on Perkin Elmer STA 6000 thermal analyzer in nitrogen atmosphere by using platinum crucible. The kinetic parameters were evaluated by utilizing thermal data with the help of Microsoft office Excel Worksheet. Here we have assumed initial decomposition temperature (T_i), half decomposition temperature (T_h), and final decomposing temperature (T_f). The point obtained at the interaction of tangent to the peak of DTG curve is called as peak temperature (T_{DTG} or T_p). As well as the decomposition temperature of polymers is recorded at 5% , 10% and 20% and mass loss (T_5 , T_{10} and T_{20}).

2.3. Method

The thermal stabilities of all the samples were measured by using thermodynamic–kinetics parameters, because kinetic study performance under the non-isothermal conditions sustained the present facts. Non-isothermal methods were extensively used for the evaluation of the kinetics and mechanism of condensed phase reactions. The thermogravimetry,



where M = Zn(II), Cd(II) and Hg(II)

Figure 1 The structure of *fbpmc* coordination polymers.

derivative thermogravimetry and differential thermal analysis techniques are powerful techniques because they are widely used to study the reaction mechanisms and kinetics of solids undergoing thermal degradation. Evaluations of kinetic parameters from thermal decomposition curves for each stage were studied from generally accepted kinetic method analysis under non-isothermal condition of thermoanalytical data that begin with Arrhenius equation. The logarithmic form of Arrhenius equation is as follows:

$$\ln K = \ln A - E_a/RT \quad (1)$$

The Arrhenius equation can be combined with the rate equation, and can be written as follows:

$$\partial\alpha/\partial t = K(T)f(\alpha) \quad (2)$$

If $f(\alpha) = (1 - \alpha)^n$ and with a constant temperature increase, $dT/dt = \beta$ (β is the heating rate in K/min), the integration Eq. (2) leads to various differential or integral methods for $n = 1$ and n not equal to zero or unity.

Out of several methods available to allow kinetic analysis of thermogravimetric data, the integral method developed by Coats–Redfern has been widely accepted as a reliable method. By using thermogravimetric data (TG/DTG/DTA) different steps of decomposition curve were subjected to find out kinetic analysis under non-isothermal condition by Coats–Redfern method.

According to *Coats–Redfern* method (Coats and Redfern, 1964) above expression can be expressed in logarithmic form where $n = 1$ and $n \neq 1$.

$$\ln \left[\frac{-\ln(1 - \alpha)}{T^2} \right] = \ln \left[\frac{AR}{\beta E_a} \left(1 - \frac{2RT}{E_a} \right) \right] - \frac{E_a}{RT} \quad (\text{For } n = 1) \quad (3)$$

$$\ln \left[\frac{1 - (1 - \alpha)^{1-n}}{T^2(1 - n)} \right] = \ln \left[\frac{AR}{\beta E_a} \left(1 - \frac{2RT}{E_a} \right) \right] - \frac{E_a}{RT} \quad (\text{For } n \neq 1) \quad (4)$$

where E_a is the activation energy (kJ mol⁻¹), α represents the fractional conversion, k is rate constant, A is the pre-exponential factor (min⁻¹), R is the universal gas constant (8.314 J mol⁻¹ K⁻¹), T is the temperature in Kelvin (K), n is

the order of reaction and t is the time (min). Using these methods (Eqs. (3) and (4)), the E_a can be estimated from the slope of a line established from fitting the TG data: $\ln \left[\frac{g(\alpha)}{T^2} \right]$ versus $\frac{1}{T}$.

The plot of $\ln \left[\frac{g(\alpha)}{T^2} \right]$ versus $\frac{1}{T}$ would give a straight line (Rocco et al., 2012). Since the order of reaction is usually not known beforehand, it is first necessary to fit the TG data with an assumed value of n . If the assumed reaction order adequately represents the reaction, the line becomes straight. If not, another reaction rate is assumed and the fitted line is examined for straightness (Tonbul and Yurdakoc, 2001; Ro et al., 2009; Al-Maydama et al., 2009). By using data obtained from Eq. (4), change in entropy (ΔS), change in enthalpy (ΔH), change in free energy (ΔG) and frequency factors were calculated by standard thermodynamic equations (Mahfouz et al., 2002).

3. Results and discussion

In the present article, the important objective was to find out the noteworthy comparative thermal stability and thermal decomposition kinetics of compounds, besides, to determine whether thermal techniques find water molecules placed at either inner or outer sphere of attraction in structure of coordination polymers. Further, thermal investigation showed higher melting points (decomposing temperatures) of polymer compounds than those of the free chelating ligand; hence, this enlightens high thermal stability of compounds.

3.1. Thermal analyses

Thermal analysis is a powerful technique, which has proved to be useful in determining the lattice, and coordinated water content in the coordination polymers, and apart from this, it is useful to determine the thermal degradation behaviors, structural aspects, and thermal stability. The matter released at each step of degradation curve was identified through attributing the mass loss at given step to the similar mass calculated from molecular formula of investigated polymer compounds, comparing that with literature values for relevant complexes considering their temperature. In the present scenario, the thermal data have exposed good thermal stability for all the synthesized coordination polymers. In fact, there are some factors that are responsible for the influence of thermal processes of decomposition such as the mass of the sample, and the multiple heating rates. Perhaps, mass of sample can determine the stability of the compound. Firstly, this can be explained based on molecular mass; the higher the molecular mass, the higher will be the melting point, which leads to greater stability. Secondly, in order to evaluate the influence of heating rate on the thermal decomposition of samples, the samples were heated to increase heating rates 5, 10 and 15 °C min⁻¹ under nitrogen atmosphere over the temperature range 28–1223 °C.

We have presented the thermographs in Figs. 2–4. After inspecting the thermal curves of compounds, it is concluded that the heating rate has a significant influence on the temperature range and shape of thermoanalytical curves. The thermal decomposition curves shifted to higher temperature range when the heating rate was increased. However, mass loss in polymer compounds at every stage does not change strongly

in distinct heating rates. The newly synthesized metal coordination polymers were found to be highly thermally stable as compared to ligand. From curves (Figs. 2–4), it is observed that the sequence of degradation that took place in these polymer compounds starts with dehydration of adsorbed water molecules followed by the release of organic fragments of the backbone. This seems like a multistage decomposition process *i.e.* thermal decomposition profile that occurs through three to four consecutive steps. The initial step of degradation at 28–150 °C may be corresponded to the removal of lattice water, at the second, third and fourth stages due to organic part of the ligand and then leaving metal oxide as a residue. Furthermore, these degraded mass losses were supported by elemental analysis and infrared data. The most important thing in the present work is that there is no weight loss within temperature range 150–200 °C. Hence, it reveals the absence of coordinated water molecules.

3.2. Thermal decomposition of coordination polymers

TG–DTG and DTA curves of compounds have been displayed in Figs. 2–4; besides, their thermal data are listed in Tables 1 and 2. In the present investigation, the structural transformation was observed with the help of thermal degradation technique, commonly called as thermogravimetry, under

controlled multiple heating rates which was further supported by DTG and DTA studies. In addition, the close investigation of thermal curves suggested the thermal decomposition profile, which occurs through multiples stages. Figs. 2–4 indicate the initial step of degradation between temperature ranges 28 and 150 °C corresponds to loss of lattice water molecules. The activation energy (E_a) for first step reaction was calculated in the range of 39–86 kJ mol⁻¹ and the releasing of adsorbed lattice water within a mention temperature range in coordination polymers was reported with good agreement (Maldonado et al., 2010; Ababei et al., 2012; Badea et al., 2012; Lin et al., 2012). From scenario (Fig. 2–4) it is also clear that the second step decomposition due to the coordinated water (150–220 °C) was almost absent. Hence, the second, third and fourth stages of decomposition *i.e.* the last step degradation profiles might be due to the organic moiety (160–1223 °C) and energy of activation for these stages was tabulated in the range of 53–474 kJ mol⁻¹.

Meanwhile, well defined TG curve of *fbpmc*–Zn(II) coordination polymer (Fig. 2) exhibits consecutive three stages of decomposition within the temperature range 38–1221 °C. The first stage at temperature range 38–158 °C with T_{DTG} peak at 61 °C corresponds to loss of two molecules of lattice water with mass loss of 7.3% (Calc. 7.1%). The activation energy for this stage was found 52.960 kJ mol⁻¹. After dehydration,

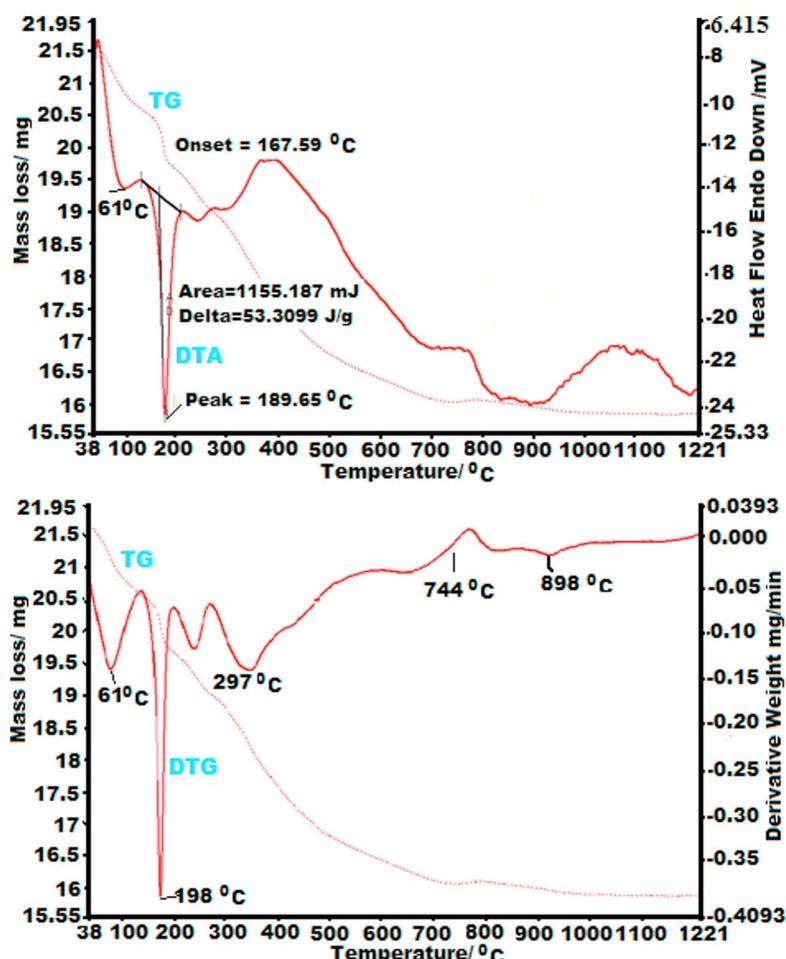


Figure 2 TG/DTA/DTG curves of Zn(II) coordination polymer.

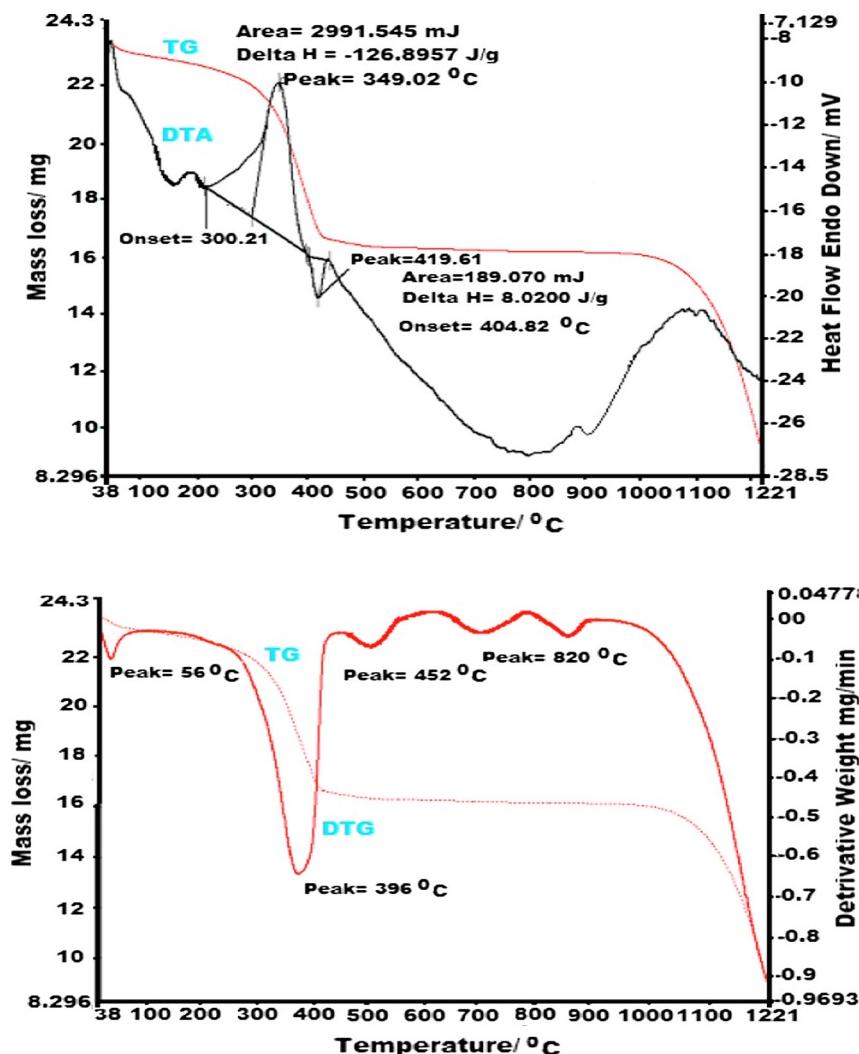


Figure 3 TG/DTA/DTG curves of Cd(II) coordination polymer.

degradation of dehydrated polymer occurred at the second and third steps due to loss of organic backbone. The second step involves the loss of two identical organic moiety C_7H_8ON -ligand fragments at temperature range 160–700 °C corresponds to the mass loss 46.4% (Calc. 48.3%) of 60% ligand with weak T_{DTG} peaks at 198, 251, 297 °C and one endothermic T_{DTA} peak at 189, 245 °C. And then, at the third step (700–1045 °C) we found two T_{DTG} peaks at 744, 898 °C might be due to mass loss 30.4% (Calc. 32.2%) of remaining 40% ligand fragments ($C_6H_2O_4N_2$) and showed two T_{DTA} peaks at 850 °C and 900 °C. No further mass loss was observed from 1045 °C to around 1221 °C because of ZnO formation which indicates a good thermal stability of this polymer. The activation energies for second and third steps were found as 111.233 kJ mol⁻¹ and 110.584 kJ mol⁻¹ respectively (Table 4–6).

On other hand, the close investigation of *fbpmpe*–Cd(II) coordination polymer (Fig. 3), shows four stages of thermal decomposition. In the first step, the degradation of polymer compound starts with dehydration from the outer sphere. This degradation started within temperature range 38–160 °C with a fine T_{DTG} peak at 56 °C and T_{DTA} peak at 58 °C of one water

molecule correspond to mass loss of 4.5% (Calc. 3.3%). The activation energy for the first step was calculated to be 86.532 kJ mol⁻¹. This process was followed by immediate loss of organic fragments from the inner sphere of polymer complex. At the second step it involves the loss of two identical organic moiety C_6H_7N -ligand fragments decomposition (288–450 °C) of 40% ligand was found mass loss of 28.6% (Calc. 30.4%) associated with a sharp long T_{DTG} peak at 396 °C and endothermic T_{DTA} peak at 419 °C and exothermic T_{DTA} peak at 349 °C. No further mass loss was observed from 450 °C to around 1050 °C, only 6.3% mass loss due to ligand, indicating a good thermal stability of this polymer. Further, in the third step (450–1050 °C) it involves the loss of another two identical organic moiety C_1H_3O -ligand fragments about 6.3% (Calc. 7.6%) associated with T_{DTG} peak at 452 °C and 820 °C of 10% ligand. The remaining 50% mass loss at fourth step within temperature range 1050–1221 °C about 36.9% (Calc. 38.1%) may be accounted for the loss of ligand fragments ($C_6H_2O_4N_2$) with T_{DTG} peak at 1107 °C and exothermic T_{DTA} peak at 1110 °C and finally leaving CdO as a residue with no further mass loss. This indicates a good thermal stability of the compound. The energies of activation were

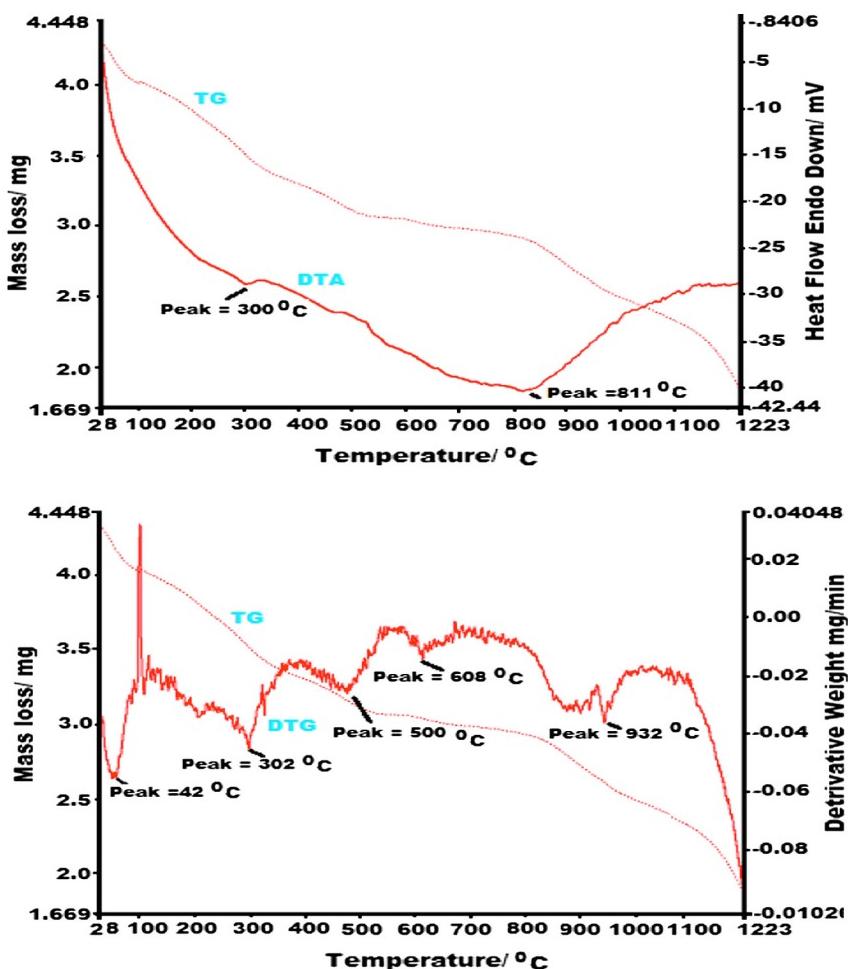


Figure 4 TG/DTA/DTG curves of Hg(II) coordination polymer.

Table 1 TG/DTG/DTA data and assignments of coordination polymers.

Polymers	Step	DTG _{max}	Temperature range (°C)	DTA (<i>T</i> _{DTA})		Weight loss	Assignment
				Endo	Exo		
Zn(II)	1st	61,118	38–158	72,120	—	7.3/7.1	–2H ₂ O (lattice water)
	2nd	198,297	160–700	—	345	46.4/48.3	–60% ligand
	3rd	744,898	700–1221	891	850,900	30.4/32.2	–40% ligand
Cd(II)	1st	56	36–160	58	—	4.5/3.3	–1H ₂ O (lattice water)
	2nd	396	288–450	419	349	28.6/30.4	–40% ligand
	3rd	452,820	450–1050	800,990	—	6.3/7.6	–10% ligand
	4th	1107	1050–1221	—	1110	36.9/38.1	–50% ligand
Hg(II)	1st	42	28–162	—	—	9.5/8.1	–3H ₂ O (lattice water)
	2nd	302,500	180–550	300	—	20.4/21.6	–35% ligand
	3rd	608,932	550–1223	811	—	37.6/40.2	–65% ligand

117.510 kJ mol⁻¹, 109.728 kJ mol⁻¹ and 474.463 kJ mol⁻¹ for the second, third and fourth steps respectively. The kinetic parameters for various steps are summarized here in Table 4–6.

Furthermore, TG/DTG/DTA curves of *fbpmpe*-Hg(II) coordination polymer (Fig. 4) represent three successive degradation stages which are shown in Table 1. The first step of thermal degradation within the temperature range 28–162 °C corresponds to three molecules of water from inner sphere of

compound with mass loss of 9.5% (Calc. 8.1%) with *T*_{DTG} peak at 42 °C. Then after, the second step thermal decomposition curve started within temperature range 180–550 °C which corresponds to two identical organic C₆H₄-ligand fragments mass loss 20.4% (Calc. 21.6%) of 35% ligand associated with two *T*_{DTG} peaks at 302 °C, 500 °C and one *T*_{DTA} peak at 300 °C. Finally, at the third step (550–1223 °C) there involves the loss of another two identical C₁H₃O- and NH₂- ligand

Table 2 Thermal stability and thermal degradation data of coordination polymers.

Polymers	TG								
	^a T_i	^b T_{\max}	^c T_f	^d T_h	^e $T_{5\%}$	^f $T_{10\%}$	^g $T_{20\%}$	^h Residue %	ⁱ LOI
Zn(II)	312	385,472,892	898	546	102	205	336	15.9	51.1
Cd(II)	315	56,396,452	1107	1122	300	310	752	23.7	48.0
Hg(II)	313	42,302,600	932	1125	85	180	355	23.5	44.5

^a The initial degradation temperature for ligand in chelate polymers.^b Peak temperature.^c Final step decomposing temperature.^d Half decomposing temperature.^e Temperature corresponding to 5% weight losses.^f Temperature corresponding to 10% weight losses.^g Temperature corresponding to 20% weight losses.^h Decomposed material left undecomposed after TGA at 1223 °C.ⁱ = LOI (limiting oxygen index).**Table 3** Activation energy and fractional conversion of coordination polymers at multiple heating rates.

Polymers	Stages	At heating rate 5 °C/min		At heating rate 10 °C/min		At heating rate 15 °C/min	
		E_a (kJ mol ⁻¹)	α	E_a (kJ mol ⁻¹)	α	E_a (kJ mol ⁻¹)	α
Zn(II)	Stage-1st	48.97777	0.044106	52.96018	0.046918	49.36853	0.043474
	Stage-2nd	110.1938	0.463603	111.233006	0.46274	105.7208	0.475501
	Stage-3rd	100.1421	0.803987	110.84172	0.843366	103.3098	0.836934
Cd(II)	Stage-1st	64.66629	0.02497	86.53211	0.006227	89.23416	0.007598
	Stage-2nd	117.75949	0.363717	117.5101	0.361724	117.5101	0.354609
	Stage-3rd	110.31846	0.487747	109.7282	0.491688	108.5975	0.490665
	Stage-4th	452.82201	0.703151	474.4634	0.635989	471.5701	0.636926
Hg(II)	Stage-1st	36.16590	0.062643	39.94877	0.049816	28.84958	0.057857
	Stage-2nd	51.38052	0.343797	53.30105	0.317593	53.10152	0.328133
	Stage-3rd	119.4222	0.73144	137.5136	0.680638	136.0586	0.688415

Table 4 Kinetic parameters in non-isothermal condition at heating rate 5 °C/min using CR equation.

Polymers	n	E_a (kJ mol ⁻¹)	$\ln A$	r^2	ΔS (J mol ⁻¹)	ΔH (kJ mol ⁻¹)	ΔG (kJ mol ⁻¹)
Zn(II)-Step-1st	2.9	48.977	16.9988	0.982	-104.501	46.2092	81.0082
Step-2nd	3.4	110.193	26.1797	0.997	-32.7369	105.446	124.139
Step-3rd	1.6	100.142	12.6498	0.999	-151.099	90.423	267.05
Cd(II)-Step-1st	1.4	64.666	22.8909	1.000	-55.3117	61.9642	79.9405
Step-2nd	5.4	117.759	23.8123	0.998	-53.6732	112.189	148.150
Step-3rd	3.7	110.318	20.9091	0.999	-78.4357	104.307	161.016
Step-4th	3.5	452.822	43.4749	0.992	103.7958	441.340	297.998
Hg(II)-Step-1st	1.7	36.165	13.1629	0.991	-135.88	33.563	76.093
Step-2nd	6.3	51.380	13.1776	0.995	-140.739	46.641	126.862
Step-3rd	3.7	119.422	15.6380	0.982	-126.479	109.437	261.338

fragments. In this step also involve $C_6H_2O_4N_2$ -ligand fragments showing two T_{DTG} peaks at 608, 932 °C with one endothermic T_{DTA} peak at 811 °C and this corresponds to release of remaining 65% ligand (Obs. 37.6% Calc. 40.2%) and finally leaving HgO as a residue with no further mass loss. This indicates a good thermal stability of the compound. The energy of activation for the first, second and third was found as 39.948 kJ mol⁻¹, 53.301 kJ mol⁻¹ and 137.513 kJ mol⁻¹ respectively. Nonetheless, further thermal stabilities were determined on the basis of thermodynamic-kinetic parameters

such as change in entropy (ΔS), change in enthalpy (ΔH), change in free energy (ΔG), frequency factor (A) and correlation coefficient (r^2) for various stages at multiple heating rates which are summarized in Table 4–6. Nevertheless, it was noteworthy observed the obtained multiple DTA/DTG peaks in polymers degradation curves; hence, this suggests that polymer compounds have well separated stages. The one more important thing was that the mass losses on DTG curves and position of DTA peaks significantly shifted toward little higher temperatures with an increase in the heating rates.

Table 5 Kinetic parameters in non-isothermal condition at heating rate 10 °C/min using CR equation.

Polymers	<i>n</i>	E_a (kJ mol ⁻¹)	$\ln A$	r^2	ΔS (J mol ⁻¹)	ΔH (kJ mol ⁻¹)	ΔG (kJ mol ⁻¹)
Zn(II)-Step-1st	2.9	52.960	18.58458	0.988	-91.3418	50.183	80.691
Step-2nd	3.4	111.233	26.42595	0.998	-30.5925	106.494	123.931
Step-3rd	1.6	110.584	13.83272	0.999	141.254	100.848	266.256
Cd(II)-Step-1st	1.4	86.532	29.50108	0.989	-0.4566	83.796	83.947
Step-2nd	5.4	117.510	23.80224	0.999	-53.7375	111.948	147.898
Step-3rd	3.7	109.728	20.84765	0.999	-78.9703	103.700	160.954
Step-4th	3.5	474.463	44.86702	0.994	115.3753	462.990	303.772
Hg(II)-Step-1st	1.7	39.948	14.2814	0.998	-126.632	37.329	77.218
Step-2nd	6.3	53.301	13.39391	0.994	-139.014	48.520	128.453
Step-3rd	3.7	137.513	17.07747	0.993	-114.540	127.495	265.515

Table 6 Kinetic parameters in non-isothermal condition at heating rate 15 °C/min using CR equation.

Polymers	<i>n</i>	E_a (kJ mol ⁻¹)	$\ln A$	r^2	ΔS (J mol ⁻¹)	ΔH (kJ mol ⁻¹)	ΔG (kJ mol ⁻¹)
Zn(II)-Step-1st	2.9	49.368	17.2936	0.999	-102.025	46.608	80.480
Step-2nd	3.4	105.720	25.2603	0.994	-40.3126	100.965	124.024
Step-3rd	1.6	103.309	13.0205	0.991	-148.038	93.565	267.066
Cd(II)-Step-1st	1.4	89.234	30.7969	0.995	10.3675	86.515	83.125
Step-2nd	5.4	117.510	23.8071	0.995	-53.7222	111.931	147.979
Step-3rd	3.7	108.597	20.6722	0.999	-80.4399	102.561	160.960
Step-4th	3.5	471.570	44.6388	0.993	113.4601	460.071	303.156
Hg(II)-Step-1st	1.7	28.849	10.2322	0.993	-160.296	26.230	76.724
Step-2nd	6.3	53.101	13.4607	0.994	-138.429	48.337	127.657
Step-3rd	3.7	136.058	17.0226	0.983	-115.017	126.015	264.955

3.3. Kinetic and thermodynamic study

Nowadays, the Coats–Redfern (CR) method has been used effectively around the world to depict the thermal decomposition kinetics mechanism of various compounds at multiple heating rates (El-Ayaan et al., 2009; Dogan et al., 2010). Keeping all this in mind here we have chosen CR method to investigate the thermal decomposition kinetics process of polymer compounds at multiple heating rates i.e., 5, 10, and 15 °C min⁻¹ as well as to find out the standard thermodynamic parameters. Thermal decomposition curves of coordination polymers shifted toward higher temperature range with increase in the heating rates; however, the mass loss and the difference between $T_{(endset)}$

and $T_{(onset)}$ did not vary with heating rates. This may be due to the different heat shifting and kinetics rates which delays degradation of compounds. From Table 4–6 it is unambiguously deduced that the first step decomposition required low E_a and this may be due to the fact that rupture of weaker bonds takes place at lower fractional conversion *i.e.* lattice water, although with increase in decomposition conversion for stronger bonds that ultimately required high E_a . Despite, by inspecting the data (Table 4–6) it reveals that the required activation energy for the releasing of ligand fragments in all polymer compounds at same steps was somewhat comparable. However, at different steps it was to be contrary because of their different kinetic mode at the transition state.

Before finding the activation energies for each stage of degradation, fractional conversion (α) values were calculated at each stage and results (Supplementary source file Table S1) suggested different mechanism for each step. After an evaluation the fractional conversion (α) of compounds plotted ' α ' versus temperature (K) in order to obtain the kinetic parameter for each degradation stage which are displayed in Figs. 5–7 (' α ' values at different stages of Cd(II) and Hg(II) are given in the Supplementary source file in Figs. S1–S7 and Table S1). Plotted curves (Figs. 5–7) shifted to a higher temperature with an increase of heating rate; hence, this verifies that thermal activation steps are occurring during degradation. It also infers ' α ' value increases as the temperature increases. Furthermore, the linearized curves of the thermal degradation have been elucidated by plotting the $\ln(g(\alpha)/T^2)$ versus $1/T$ which gives a straight line with slope equal to $-E_a/R$ and the activation energies were calculated from obtained slope. The CR plots ($\ln(g(\alpha)/T^2)$ versus $1/T$) for each stage of degradation were constructed for E_a of Zn(II) polymer and are

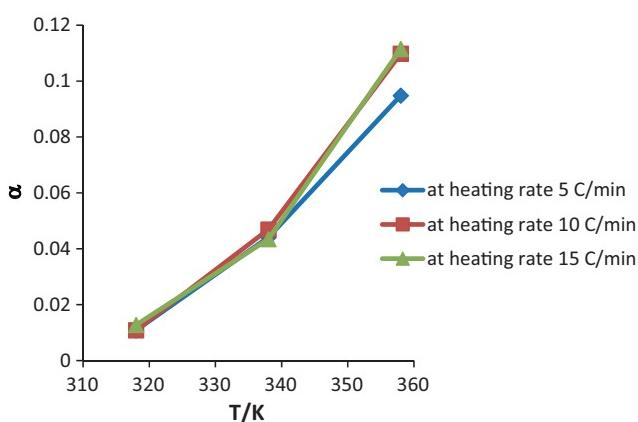


Figure 5 Plot of fractional conversion versus temperature for first stage decomposition of Zn(II) coordination polymer.

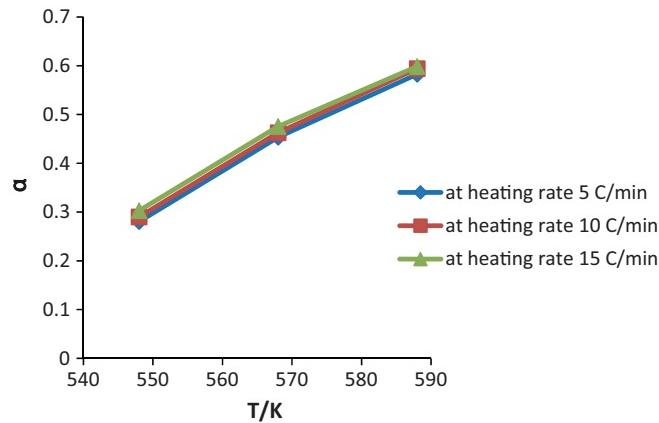


Figure 6 Plot of fractional mass loss versus temperature for second stage decomposition of Zn (II) coordination polymer.

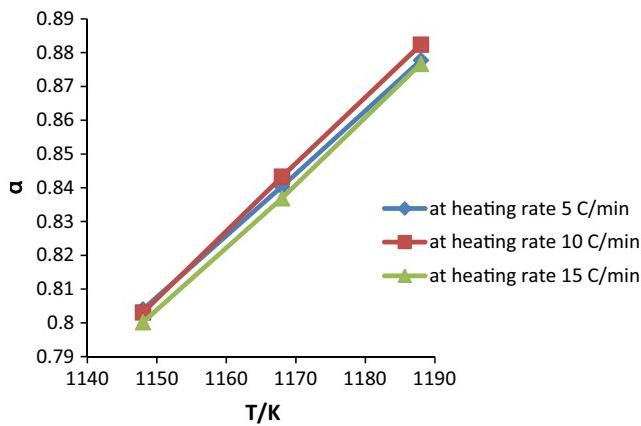


Figure 7 Plot of fractional mass loss versus temperature for third stage decomposition of Zn(II) coordination polymer.

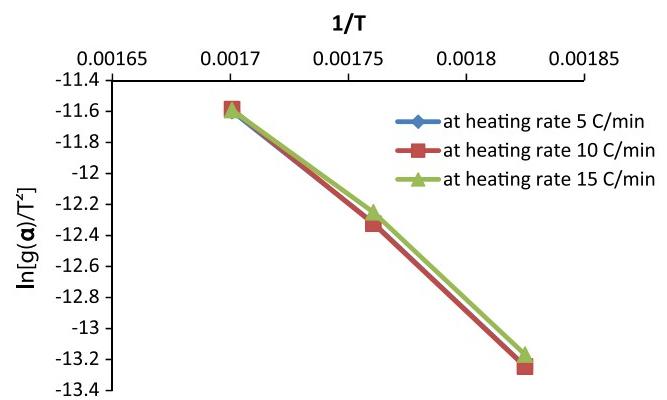


Figure 9 CR plots for evaluation of E_a of second stage of *fbpmc*-Zn(II) in nitrogen atmosphere.

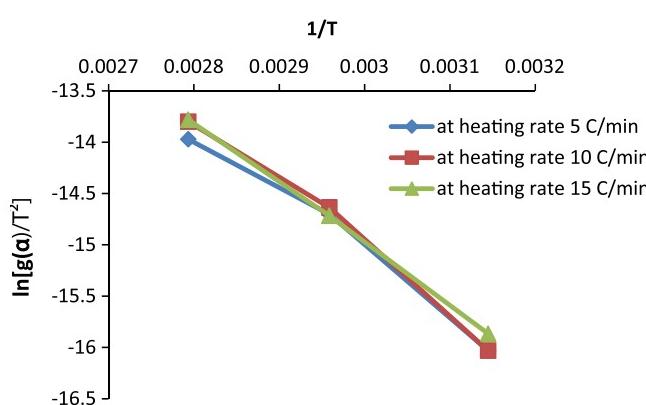


Figure 8 CR plots for evaluation of E_a of first stage of *fbpmc*-Zn(II) in nitrogen atmosphere.

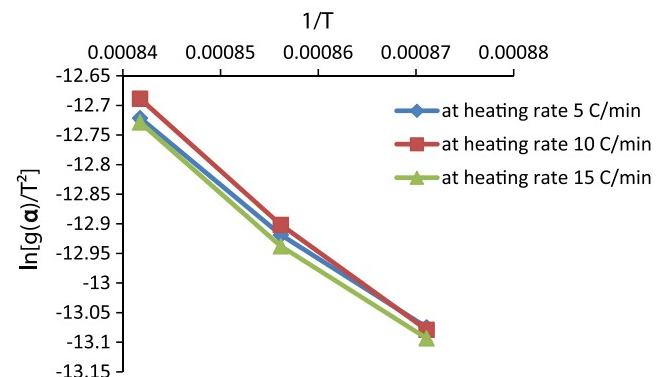


Figure 10 CR plots for evaluation of E_a of third stage of *fbpmc*-Zn(II) in nitrogen atmosphere.

presented in Figs. 8–10 (CR plots for different stages of Cd(II) and Hg(II) compounds are given in the supplementary source file in Figs. S8–S13 and Table S1). The correlation coefficients (r^2) of linearized curves were found approximately 0.982–1.00. Therefore, it was concluded that E_a with more consistent, comparable, and excellent value from multiples heating rates.

A further change of activation energies with fractional conversion indicates polymer process involving more than one-step and when the curves for all three stages were compared to each other, their shapes indicate a different mechanism.

Moreover, plotted activation energy versus fractional conversion of coordination polymers at multiple heating rates is shown in Figs. 11–13 and tabulated in Table 3. From Fig. 11 Zn(II) and Table 3 it clearly reveals that there is an increase

and smoothly decrease of activation energy as the reaction proceeds. In this case, E_a increases in the range of 40–60 kJ mol⁻¹ for $\alpha = 0.04$, reaching maximum of 105–111 kJ mol⁻¹ at $\alpha = 0.463$, and then decreases smoothly to 110–100 kJ mol⁻¹ at $\alpha = 0.843$. The observed convex shape is due to dehydration at lower E_a . Further dehydrated compound detached into two identical C₇H₈ON-ligand fragments at higher E_a and subsequently removed remaining C₆H₂O₄N₂-ligand fragments at medium E_a .

However, degradation of Cd(II) (Fig. 12) increases E_a from first step to second step and slightly decreases from second step to third step and at the last step it increases tremendously. In the commencement, the activation energy was 64–89 kJ mol⁻¹ at $\alpha = 0.0062$ –0.024. It increases fairly, reaching about 117 kJ mol⁻¹ at $\alpha = 0.36$, then it decreases slowly about 108–110 kJ mol⁻¹ at $\alpha = 0.48$ –0.89 and lastly rises sharply to 454–474 kJ mol⁻¹ at $\alpha = 0.6$ –0.7. This indicates a complex mechanism involving parallel and multi-steps reactions. In this case also, dehydration of compound started at lower E_a , further dehydrated polymer compound separated into two identical organic moiety C₆H₇N-ligand fragments at higher E_a , then losses of another two identical C₁H₃O-ligand fragments at average activation energy and finally losses remaining C₆H₂O₄N₂-ligand fragments at elevated activation energy.

In the next compound Hg(II) (Fig. 13), the dependence of activation energy on conversion degree is shown similar to Cd(II) mechanism, and the E_a increases during the entire process at different degree conversion. In the beginning the activation energy was 28–39 kJ mol⁻¹ at $\alpha = 0.049$ –0.062. It increases steadily, reaching at 53 kJ mol⁻¹ at $\alpha = 0.32$, and then it rises enormously to 119–136 kJ mol⁻¹ at $\alpha = 0.73$. This specifies a complex mechanism concerning multi-steps reactions. In this case also, dehydration of polymer compound started at lower E_a , further dehydrated compound losses two identical C₆H₄-ligand fragments at higher E_a , then it involves the loss of another two identical C₁H₃O- and NH₂-ligand fragments, along with C₆H₂O₄N₂-ligand fragments at high activation energy.

Interestingly Tables 3–6 show the highest activation energies to entire heating rates at the second and last steps as compared to first step for Hg(II) (53.301 and 137.513 kJ mol⁻¹), Cd(II) (117.510 and 474.463 kJ mol⁻¹) and Zn(II) (111.233 and 110.584 kJ mol⁻¹) which may be due to the thermal decomposition of ligand fragments. In addition, these activation energies are noteworthy supported by free energy change. Likewise, ΔG for the second and last steps (for Hg(II) 128.453 and 265.515 kJ mol⁻¹, for Cd(II) 147.898 and 303.772 kJ mol⁻¹ and for Zn(II) 23.931 and 266.256 kJ mol⁻¹ respectively) is higher than the first step (for Hg(II) 77.218 kJ mol⁻¹, for Cd(II) 83.947 kJ mol⁻¹ and for Zn(II) 80.691 kJ mol⁻¹).

On the other hand, the first stage decomposition corresponded to loss of lattice water where its energy of activation was calculated as $E_a = 39.948$ kJ mol⁻¹ for Hg(II), $E_a = 86.532$ kJ mol⁻¹ for Cd(II) and $E_a = 52.960$ kJ mol⁻¹ for Zn(II). Thus, it indicates that the thermal stability was higher at second and last steps that might be due to the slow degradation of ligand fragments in coordination polymers and eventually formation of metal oxide. A low value obtained at the first stage might be due to the weakly bonded lattice water to polymer compound. Perhaps, in the first step there requires low E_a value and this is because the rupture of weaker

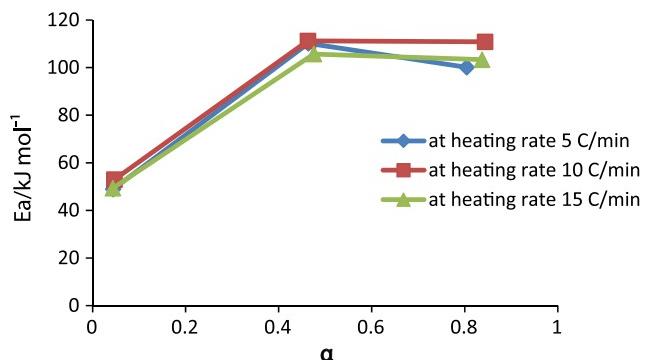


Figure 11 Plot of E_a versus α for all the stages of Zn(II) coordination polymer at heating rate 5, 10, and 15 °C/min.

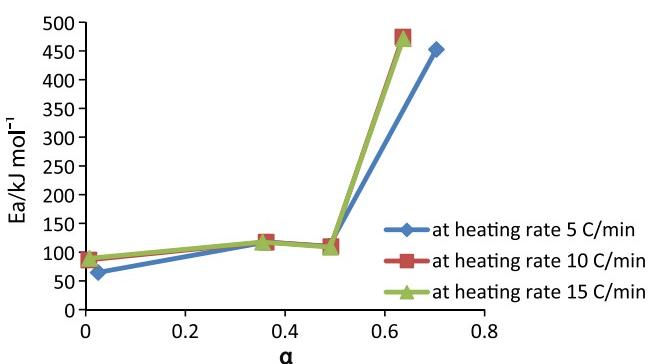


Figure 12 Plot of E_a versus α for all the stages of Cd(II) coordination polymer at heating rate 5, 10, and 15 °C/min.

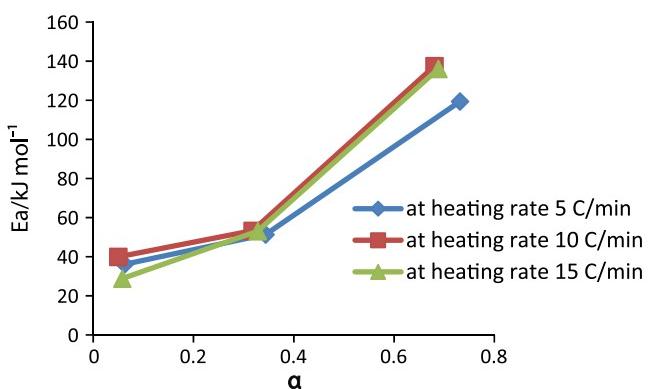


Figure 13 Plot of E_a versus α for all the stages of Hg(II) coordination polymer at heating rate 5, 10, and 15 °C/min.

bonds (lattice water), but with increase in decomposition conversion with stronger bonds will ultimately require high E_a . Besides, It was also supported by getting low value of ' $\ln A$ ' for first step and high value of ' $\ln A$ ' for higher steps.

Hence, it must be stated that the higher the E_a value, the slower the decomposition process. Especially, the E_a values are most helpful in assigning the strength of compounds. Therefore, it is right to say that the slow elimination of ligand is with higher activation energy and rapid one is with lower activation energy. Furthermore, entropy change values were

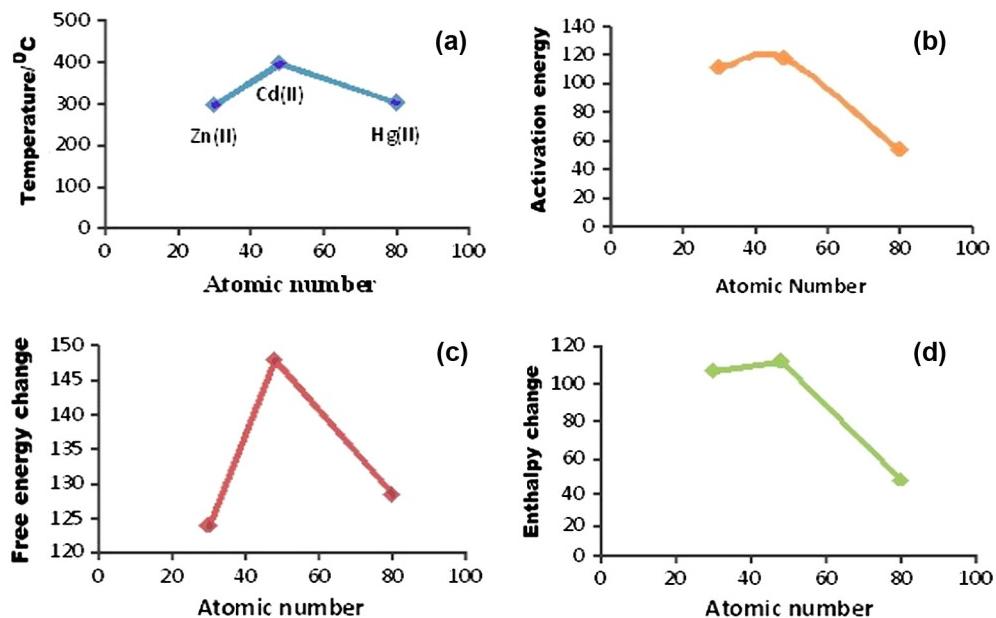


Figure 14 Plots of kinetic parameters of coordination polymers versus atomic number at the second stage decomposition at heating rate 10 °C/min: (a) initial decomposition temperature (ligand), (b) activation energy, (c) free energy change, and (d) enthalpy change.

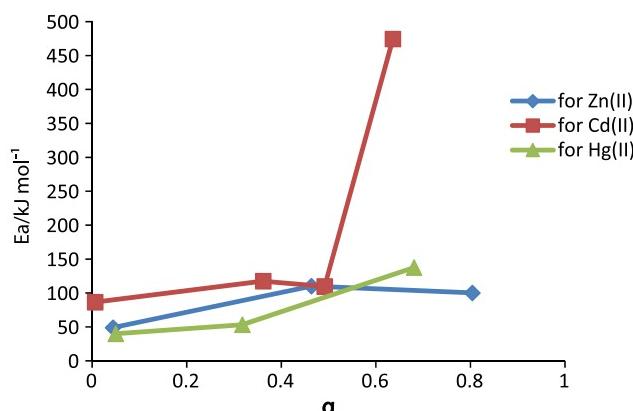


Figure 15 Comparative plot of E_a versus α for all the degradation stages of coordination polymers at heating rate 10 °C/min.

obtained at few steps with high positive values. So, polymer compounds can be believed to be less ordered structures than reactant. Despite, obtained negative values of entropy change for maximum steps of decomposition ($\Delta S = -0.4566 \text{ J mol}^{-1}$ to $-139.014 \text{ J mol}^{-1}$) which corresponded to the more ordered reaction and suggested decomposition reactions slower than normal and non-spontaneous nature of reaction (Swaney and Bansal, 1983; Kharadi, 2012; Refat et al., 2010). The non-spontaneous degradation behaviors of compounds were supported by getting high positive values of ΔG . This recommended the high thermal stability of polymer compounds (Boonchom, 2009; Ahmed, 2007). As well as obtained high positive ΔH values indicate the decomposition process was endothermic in nature. Hence, overall the kinetic and thermodynamic parameter studies were significantly helpful for the elucidation of non-spontaneity and thermal stability of coordination polymers.

Apart from this, the plotted kinetic parameters of coordination polymers versus atomic number at the second stage decomposition at heating rate 10 °C/min are used to find out the comparative order of stability. The order of kinetic stability obtained from Fig. 14a-d was in good agreement and suggests the highest order of thermal stability to Cd(II) ion. Despite the thermal stability it also checks out from the char residue yield (Table 2). Higher the value of residue yield, higher will be thermal stability (Arora et al., 2013). Further, it was also an important to plot the kinetics versus fractional conversion for all the degradation stages of coordination polymers to check out comparative thermal stability (Fig. 15). From Fig. 15 curves reflect that Cd(II) required activation energy for first step degradation at $\alpha = 0.006227$ is $86.532 \text{ kJ mol}^{-1}$, for second step degradation at $\alpha = 0.361724$ is $117.510 \text{ kJ mol}^{-1}$ and for final fourth step degradation at $\alpha = 0.635989$ is $474.463 \text{ kJ mol}^{-1}$ than other

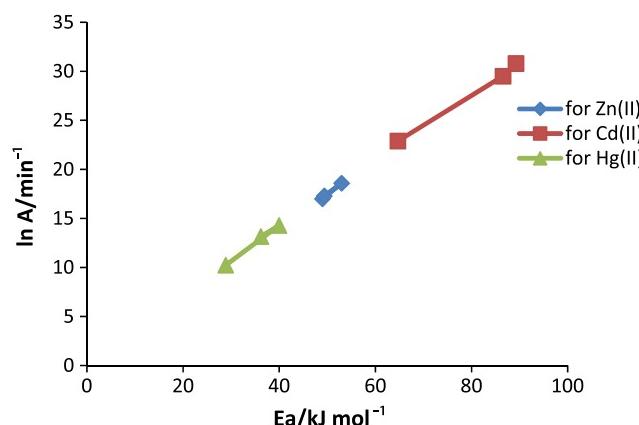


Figure 16 Plot of $\ln A$ versus E_a for 1st stage degradation of coordination polymers at heating rate 5, 10, and 15 °C/min.

metal ions. Therefore, on the basis of above thermal degradation behaviors (TG/DTG/DTA), thermal data, initial, and final decomposition temperatures, plotted various curves, and thermodynamic–kinetics parameters, the metal coordination polymers were found to be thermally stable; however, Cd(II) shows superior stable than other metal ions. Consequently, on the basis of above kinetics parameters values and plots (Figs. 11–16) the order of thermal stability of metal coordination polymers is as follows: Cd(II) > Hg(II) > Zn(II). Studies show that Cd(II) coordination polymer was more stable than others. With this a trend further plotted the dependence in A versus activation energy for first step of degradation and obtained the linear dependences, and again curve reflects more stability to cadmium ion.

4. Conclusions

In a summary, we have reported comparative thermogravimetric study of three metal coordination polymers of fumaroyl *bis* (paramethoxyphenylcarbamide). We performed thermal study including thermal behaviors, the influence of multiple heating rate and thermodynamic–kinetic determination under the nitrogen atmosphere in non-isothermal conditions. A significant outcome of the heating rate on the thermal decomposition of coordination polymers was examined at the second and last stages. The thermal decomposition investigations were helpful to confirm the presence of number and nature of water molecules in coordination polymers. Thermal decomposition of coordination polymer was a stepwise process involving one-step of dehydration from outer sphere and two–three steps of degradation of ligand from inner sphere of dehydrated coordination polymers. The TG curves show the mass decreases with linear increase in temperature. The observed percentage of mass loss, corresponding to the various steps in the thermogravimetric curves was compared with those calculated in the assumption of possible composition of the polymer compounds suggested from the elemental analysis and later confirmed from spectral analysis. The transformation in each step causes changes in the structure and chemical composition of coordination polymers.

After comparing the thermal curves, the temperature ranges of decomposition and value of kinetic parameters were found higher for E_a , ΔG , and A , and lower for k in case of all polymer compounds; therefore, it was concluded that these compounds may be called as thermally stable materials. The thermodynamic–kinetic triplet obtained for each stage of decomposition reaction reflects the mechanism related to definite characteristic of system under study. The activation energies were obtained by assuming order of reaction under Coats–Redfern method by using TG/DTG and DTA data, where Cd (II) shows highest values of activation energy as compared with others. Positive values of ΔG and negative value of ΔS reflect the high thermal stability and non-spontaneous decomposition behaviors of the polymer compounds. However, the negative values of entropy changes indicate that the dehydrated coordination polymers have a more ordered structure and the reactions are slower than normal.

Based on the decomposition temperature, thermal decomposition kinetic parameters, and char residue values, the order of thermal stability was found as Cd(II) > Hg(II) > Zn(II). Interestingly, in this study we have found better thermal stability at higher steps than at lower steps because of slow degradation of ligand fragments at higher step.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.arabjc.2016.03.008>.

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